# PH EFFECTS ON THE ENERGETICS OF IRRADIATED TiO₂ SUSPENSIONS IN AQUEOUS D-GLUCOSE

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RÉSUME. — Les photocourants anodiques et les quantités d'hydrogène produits lors de l'irradiation (350 < \( \lambda < 420 \, nm \) de suspensions aqueuses de particules de TiO₂ contenant 0,5 % (en poids) de D-glucose ont été mesurés à différentes valeurs du pH. L'influence des valeurs du pH initial sur les vitesses de variation du photocourant avec le temps,  $\Delta i/\Delta t$ , et sur les vitesses de production de l'hydrogène avec le temps ont été examinées afin d'obtenir des informations sur l'énergétique des photocatalyseurs de TiO2 ayant des dépôts de Pt et RuO<sub>2</sub> à leur surface. Le transfert des électrons produits par la lumière vers les dépôts de platine et la consommation ultérieure de cette charge lors de la formation d'hydrogène dépend fortement de la concentration des protons en solution. Des solutions acides (pH2) doivent être utilisées pour assurer le dégagement d'hydrogène dans les suspensions de TiO2 mélangées avec des catalyseurs Pt/SiO2, dont les dépôts de platine sont cathodiquement chargés grâce à un transfert inter-particules des électrons produits par la lumière sur les particules de TiO2. Les dépôts de platine à la surface des particules de TiO2 sont beaucoup plus efficaces pour collecter les électrons : des quantités plus élevées d'hydrogène ont été observées à toutes les valeurs du pH et notamment dans les milieux alcalins où l'action du D-glucose en tant que consommateur de trous est favorisé par une concentration plus élevée en ions OH-. Des études photoélectrochimiques et photocatalytiques conjointes sont nécessaires pour équilibrer la production des électrons (et des trous) sur les surfaces des smiconducteurs illuminés, avec la consommation de ces charges à la surface du catalyseur.

ABSTRACT. — The anodic photocurrents and the amounts of  $H_2$  produced under irradiation (350 <  $\lambda$  < 420 nm) of aqueous suspensions of TiO<sub>2</sub> particles containing 0.5 wt.% D-glucose were measured at various pH values. The influence of the initial pH values on the rates of change of photocurrent with time,  $\Delta i/\Delta t$ , and on the rates of  $H_2$  production with time was examined to obtain information on the energetics of TiO<sub>2</sub> photocatalysts with Pt and RuO<sub>2</sub> deposits. The transfer of photoproduced electrons to platinum deposits and the subsequent consumption of this charge for  $H_2$  formation strongly depends upon the proton concentration in solution. Acidic solutions (pH 2) are necessary for  $H_2$  evolution with TiO<sub>2</sub> dispersions mixed with Pt/SiO<sub>2</sub> catalysts, where the platinum deposits are cathodically charged through intra-particle electron transfer of the photoproduced electrons on TiO<sub>2</sub> particles. Platinum depositions on the TiO<sub>2</sub> particles themselves are much more efficient in collecting electrons; larger amounts of  $H_2$  were produced at all pH values and especially in alkaline media where the hole scavenging action of D-glucose is also favored by a higher concentration of OH<sup>-</sup> ions. A combination of photoelectrochemical and photocatalytic studies is useful in determing the balance between electron (and hole) production on illuminated surfaces of the semiconductors and consumption of these charges on the catalyst surface.

# Introduction

Recently the pH dependence of the photocurrent produced at an inert electrode during the photooxidation of various polyalcohols or sugars by illuminated TiO<sub>2</sub> suspensions have shown that a significant increase of their hole scavenging efficiency occurs with an increase in the initial OH-concentration <sup>1, 2</sup>. When the photogenerated electrons are scavenged by a pH independent redox couple such as MV<sup>2+</sup> (methyl viologen) and the holes by an organic material in a reaction producing protons, the pH of the medium decreases during illumination. Under these conditions the anodic photo-

currents for these aqueous mixtures decrease slowly during continuous illumination. The maintenance of an optimal pH value for a high photoactivity can be realized by the use of an appropriate catalyst capable of removing the protons produced in the anodic reaction as H<sub>2</sub> and to keep the initial pH constant.

The investigation of particulate TiO<sub>2</sub> photocatalysts by the electrochemical methods recently described <sup>3-5</sup> in which photogenerated electrons are collected on an inert electrode can be combined with GC measurements of the H<sub>2</sub> produced in the same suspensions. In this work we describe these types of experiments that were carried out to obtain more insight

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about the photocatalytic properties of TiO<sub>2</sub> particles with various catalytic deposits.

D-glucose was chosen as the hole scavenger because of its efficiency <sup>2</sup> and because it is the principal component of different inexpensive biomasses that have been investigated <sup>6</sup> for the conversion of their chemical energy into H<sub>2</sub> or electricity via photocatalytic reactions. Among the recent electrochemical and photochemical investigations on the electrocoxidation (on Pt electrodes) <sup>7</sup> and respectively on the photofermentation <sup>8</sup> or the photocoxidation (on Pt/TiO<sub>2</sub> particles) <sup>6</sup> of D-glucose, none has described the influence of pH on these mechanisms except in some preliminary studies of polyalcohols <sup>1, 2</sup> and sugars <sup>2</sup> in TiO<sub>2</sub> suspensions.

#### **Experimental**

#### COMPOUNDS

Reagent grade chemicals H<sub>2</sub>PtCl<sub>6</sub> (Aldrich), RuO<sub>4</sub> (Alfa), and methyl viologen chloride (Sigma Chemical Co.) were used as received. Deionized, doubly-distilled water was used to prepare all solutions.

 $TiO_2$  (Degussa P25) powder having a negligible pore volume, a high anatase content and a BET area of  $55\,\mathrm{m}^2\,\mathrm{g}^{-1}$  was used. The  $Pt/TiO_2$  and  $Pt/SiO_2$  catalysts were prepared as previously described 9 by impregnating 50 ml of stirred suspensions of  $1\,\mathrm{g}\,TiO_2$  (Degussa P25) or  $1\,\mathrm{g}\,SiO_2$  (Degussa) with the required amount of a 10% chloroplatinic acid solution. After evacuation at  $350\,\mathrm{K}$  and drying in an oven at  $400\,\mathrm{K}$ , the powder was flushed with  $N_2$  in a Pyrex tube with the temperature increased to  $573\,\mathrm{K}$  and then reduced in  $H_2$  at  $750\,\mathrm{K}$  for 15 hours.

RuO<sub>2</sub>/TiO<sub>2</sub> catalysts were prepared by introducing the required amount of RuO<sub>4</sub> in 100 ml of a stirred suspension of 5gTiO<sub>2</sub> followed by 2 hours heating at 325 K in a closed flask <sup>12</sup>. Half of this suspension was loaded with platinum using the photodeposition technique <sup>10, 11</sup>: the calculated amount of H<sub>2</sub>PtCl<sub>6</sub> was added to the RuO<sub>2</sub>/TiO<sub>2</sub> suspension and irradiated with UV light for 10 minutes. The presence of Pt and Ru on the TiO<sub>2</sub> and SiO<sub>2</sub> particles was detected qualitatively by X-ray photoelectron spectroscopic and X-ray microprobe techniques. Less than 1% (by weight) quantities of Pt and RuO<sub>2</sub> were used to maintain high activity, but no attempt was made to maximize the photocatalytic activity of the particulate systems.

#### APPARATUS

Photoelectrochemical experiments were performed in a two-compartment Pyrex cell divided by a fine porosity glass frit. The larger compartment (100 ml solution volume) was equipped with a port for placement of a Beckman combination pH electrode and a flat optical window sufficiently large to allow illumination of the entire area of the TiO<sub>2</sub> suspension in the chamber. The collector electrode, a gold flag (10.6 cm<sup>2</sup>), was placed in the slurry compartment near a saturated calomel electrode (SCE) used as a reference electrode. The counter electrode, a large platinum flag, was placed in the compartment separated from the slurry.

The pH of the suspension, adjusted to the desired values by addition of small amounts of either 1.0 N H<sub>2</sub>SO<sub>4</sub> or 1.0 N NaOH, was measured with a Corning Model 12 pH meter. Photocurrents were recorded with a Princeton Applied Research Model 173 potentiostat/galvanostat and a Houston Instruments model 2000 X-Y recorder.

The illumination source was a 3.0 kW Xe arc lamp (Christie Corp., Los Angeles, CA., Model VF 30 K K) operated at 1.6 kW. In all experiments, a 10 cm water bath was used to remove IR radiation and a 350 nm cut-off filter to prevent the direct photolysis of methyl viologen 13. 16.

A 55ml Pyrex flask, filled with 40ml of suspension whose pH was initially adjusted to the desired value, was used in GC measurements of the amounts of photogenerated of H<sub>2</sub>. After 1 hour of

degassing with prepurified nitrogen, the samples, stirred at constant speed, were irradiated at  $350 < \lambda < 420$  nm. Gas aliquots (50 to 200 µl taken from 15 ml of gas phase) were analyzed by gas chromatography (Autoprep. A-700) with a 15 foot Porapak column at room temperature. No hydrocarbons (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, etc.) or CO<sub>2</sub> were observed. The main product of long term photooxidation of D-glucose on TiO<sub>2</sub> particles is a mixture of aldehydes and ketones having 6 C atoms. The chemical analysis has shown the presence of >C=O and >CHO functions, but the attempt to identify by GC-MS the identity of these compounds was unsuccessful.

#### Results and discussion

Illuminated suspensions of TiO<sub>2</sub> (2.5 g.1<sup>-1</sup>) in aqueous 0.1 wt.% D-glucose at an initial pH9 produced small anodic photocurrents ( $\sim 3 \mu A$ ) at a gold (10.6 cm<sup>2</sup>) electrode immersed in the stirred suspension. These anodic photocurrents result from the production of electron-hole  $(e^-h^+)$  pairs under irradiation at  $350 < \lambda < 420 \,\mathrm{nm}$  and the partial consumption of holes by an electron donor like D-glucose, followed by the collection of electrons at the inert electrode 3. This photocurrent, always independent of the position and the orientation of the collector electrode, originates from charges on the bulk suspension. Its value decreased to essentially zero if stirring was stopped. The direct collection of electrons (existing for instance as Ti3+ centers) on the particle surface by the inert electrode is rather inefficient because the rate of  $e^-h^+$  recombination increases as the electrons build up on the particles. The current is low and reaches a maximum value of  $\sim 3 \,\mu A$  in less than 2 minutes.

The addition of small amounts of methyl viologen dication (MV<sup>2+</sup>), an efficient electron trapping agent <sup>1, 5</sup> capable of reacting with the photogenerated electrons to form the reduced radical MV+\* that is oxidizable at the collector electrode, significantly increased the photocurrent. Under illumination, the anodic photocurrent grew to values near 1 mA, concomitant with the appearance of the blue color of MV+ radical. When the light was removed, the anodic photocurrent persisted and decayed slowly to zero as MV \*\* was oxidized at the collector electrode 5. Generally, stirred suspensions are rather opaque so that TiO<sub>2</sub> particles are illuminated only when they pass close to the illuminated window. The use of an efficient hole scavenger is therefore necessary to decrease the rate of  $e^-h^+$  recombination and to allow the storage of the negative charge until it is trapped by an electron acceptor like methyl viologen or, as discussed later, by a catalytic deposit where this charge is consumed.

The use of a same concentration of  $MV^{2+}$ , chosen so that  $[MV^{+'}] \leqslant [MV^{2+}]$  in all experiments was necessary to maintain an excess of the electron trapping agent with respect to the electrons available on the surface of  $TiO_2$  particles. The rate of photocurrent increase,  $\Delta i/\Delta t$ , measured as initial slope on the photocurrent-time curves, was always determined for  $[MV^{2+}] = 10^{-3}$  M, the other experimental conditions, i. e., light intensity, cell geometry, quantity of  $TiO_2$  and of D-glucose, area and imposed potential of working electrode, speed of stirring, temperature, pH, were held constant unless otherwise specified.

During the continuous illumination, the pH becomes progressively lower and follows a similar time dependence (see curves 1 and 2 in Figure 1) as that of the photocurrent-time dependence simultaneously recorded. As previously reported, the consumption of the photoproduced holes,  $h^+$ , by alcohols <sup>10, 15</sup>, polyalcohols <sup>1, 2</sup> or sugars <sup>2</sup> according to the suggested mechanism <sup>10, 15</sup>:

$$>$$
CHOH $+h^+ \rightarrow >$ CO $+H^++H^*(orH^++e^-)$  (1)

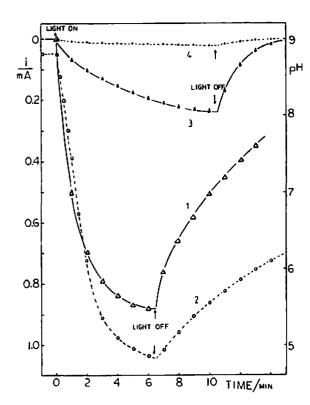


Figure 1. – Photocurrent vs. time ( $\triangle$ ,  $\triangle$ , full line, left scale) and pH vs. time ( $\bigcirc$ ,  $\odot$ , dotted line, right scale) dependences for: (1)  $\triangle$ , (2)  $\bigcirc$ , 0.25 g TiO<sub>2</sub> and (3)  $\triangle$ , (4)  $\odot$ , 0.25 g TiO<sub>2</sub> + 0.25 g Pt (0.63 wt. %)/SiO<sub>2</sub> suspensions. Cell conditions: gold electrode (10.6 cm<sup>2</sup>) held at 0.2 V/SCE, D-glucose 0.5%, MV<sup>2+</sup> 10<sup>-3</sup> M, 100 ml Na<sub>2</sub>SO<sub>4</sub> 0.0325 M.

depends upon the initial quantity of OH" ions in the bulk. Hydrogen ions produced during the above reaction significantly decreased the initial pH value of neutral suspensions, except when H<sub>2</sub> was formed by using an appropriate catalyst. Effectively, the initial pH was almost constant (see curve 4 in Figure 1) when a mixture of  $0.25 \,\mathrm{g\,TiO}_2 + 0.25 \,\mathrm{g\,Pt}$ (0.63 wt. %)/SiO<sub>2</sub> was irradiated under the same experimental conditions. Platinum deposits supported by silica can collect the negative charge produced on the TiO2 particles (or on the existing MV+ radicals) and to reduce H+ ions produced during the photooxidation of D-glucose. The photocurrent observed in the presence of Pt/SiO<sub>2</sub> is significantly smaller (see curve 3 in Figure 1) because photogenerated electrons produce H<sub>2</sub> rather than being collected at the inert collector electrode. No anodic photocurrent was observed when a higher (>0.3 g) quantity of Pt (0.63 wt. %)/SiO<sub>2</sub> was used. Blank experiments on TiO<sub>2</sub>+SiO<sub>2</sub> mixed suspensions have shown only a slight decrease of the photocurrent compared to that for TiO2 alone, probably because the silica particles obscure the light when they pass close to the illuminated window.

The hole scavenging efficiency of D-glucose was markedly influenced by its concentration when it was lower than 0.5 wt. % (see Fig. 2). The dependence of the  $\Delta i/\Delta t$  values with the initial pH was almost the same for suspensions containing 0.5 or 1 wt. % glucose. In all following experiments we used suspensions containing 0.5 wt. % glucose.  $\Delta i/\Delta t$  vs. pH curves were similar for 0.5 wt. % D-glucose and for 0.5 wt. % D-sorbitol. The magnitude of photocurrents and of  $\Delta i/\Delta t$  values at pH < 9 has shown that D-sorbitol, which has 6 hydroxyl groups is a more efficient hole scavenger than D-

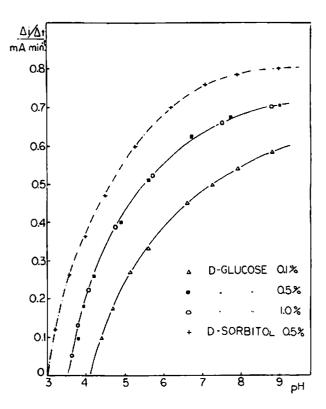


Figure 2. — Dependence of the rate of the change of photocurrent with time  $(\Delta i/\Delta t)$  vs. pH for TiO<sub>2</sub> 2.5 g.l<sup>-1</sup> suspensions containing D-glucose and D-sorbitol. Same cell conditions as Figure 1.

glucose, which has only 5 > CHOH groups. On the contrary, at pH > 10 the efficiency of D-glucose becomes greater than that of D-sorbitol<sup>2</sup> as a result of the transformation of its aldehyde groups into two hydroxyl groups. To avoid this complication, only pH values lower than 10 were used in all following experiments.

The increase of photocurrent and  $\Delta i/\Delta t$  values when the initial concentration of OH<sup>-</sup> ions increased (pH < 10) shows that hole consumption by D-glucose is favored by an increase of OH<sup>-</sup> in the bulk. An obvious reason is the neutralization of H<sup>+</sup> produced in reaction (1) by OH<sup>-</sup>.

The (0.43 wt. %) RuO<sub>2</sub> deposits on TiO<sub>2</sub> particles significantly decreased the  $\Delta i/\Delta t$  values and shifted the intercept on pH axes slightly towards more acidic values (see Fig. 3). Apparently, the presence of RuO<sub>2</sub> on TiO<sub>2</sub> surface favors electron consumption as H<sub>2</sub> even more than Pt/SiO<sub>2</sub> does. Thus, when 0.1 g of platinum loaded silica was mixed with 0.25 g of TiO<sub>2</sub>, a decrease of  $\Delta i/\Delta t$  values was also observed, but the intercept of the  $\Delta i/\Delta t$  vs. pH plot with the pH axis was shifted towards more basic values (see curve 2 in Figure 3). The difference in the pH intercept for these two cases probably reflects the differences in the rates of the catalyzed reaction of MV<sup>++</sup> with H<sup>+</sup> and of the reaction of holes with D-glucose.

The amount of  $H_2$  evolved in such a mixture of  $TiO_2$  particles with Pt loaded  $SiO_2$  suspended in aqueous D-glucose was strongly dependent upon the initial pH value (see Fig. 4). Both the quantity of  $H_2$  produced and the rate of its production with time of illumination show maximum values for pH 2. The inter-particle electron transfer involved in the mixed  $TiO_2 + Pt/SiO_2$  suspensions and the catalyzed  $MV^{++}$ -proton reaction is favored in acidic solutions. At pH 7,  $H_2$  evolution is low because of a low concentration of protons in the bulk solution. At high proton concentrations (e. g.,

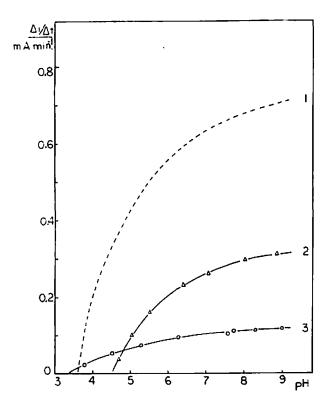


Figure 3.  $-\Delta i/\Delta t$  vs. pH dependence for various suspensions containing 0.5 wt. of D-glucose. (1) 0.25 g TiO<sub>2</sub> Degussa P25, (2) 0.25 g TiO<sub>2</sub> + 0.1 g Pt (0.63 wt. %)/SiO<sub>2</sub>, (3) 0.25 g RuO<sub>2</sub> (0.43 wt. %)/TiO<sub>2</sub>. Same cell conditions as Figure 1.

pH 1.1) the rate of H<sub>2</sub> production is decreased, probably because of the greatly decreased rate of hole scavenging by D-glucose, as discussed earlier.

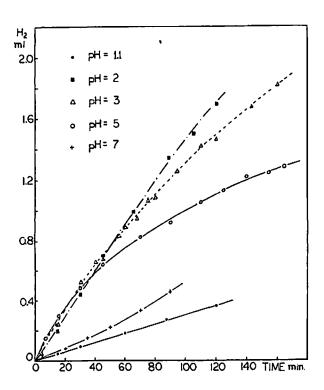


Figure 4. — H<sub>2</sub> production as a function of illumination time for suspensions (40 ml) of 0.1 g TiO<sub>2</sub>+0,1 g Pt (0.63 wt. %)/SiO<sub>2</sub> in aqueous glucose 0.5 wt. % containing 10<sup>-3</sup> M MV<sup>2+</sup>, at various pH values.

A comparison of the  $H_2$  production-time dependences shown in Figure 4 with  $\Delta i/\Delta t$  values in Figure 3 suggests that a lack of photocurrent at pH values more acidic than the intercepts of  $\Delta i/\Delta t$  vs. pH curves on pH axis doesn't necessarily mean that there is no photoactivity.

The electron trapping efficiency of methyl viologen strongly depends upon its concentration<sup>5</sup> and on the reoxidation of MV<sup>+\*</sup> radicals at the collector electrode. Similarly, the electron transfer to platinum deposits depends upon the number of silica particles loaded by Pt and on the rate of H<sub>2</sub> evolution at these catalysts, i. e., on the quantity of H<sup>+</sup> in the bulk. No H<sub>2</sub> was observed for mixtures without D-glucose at pH 2 or for irradiation of Pt/SiO<sub>2</sub> particles in the absence of TiO<sub>2</sub> particles.

The presence of MV<sup>2+</sup> had little influence on the amount of H<sub>2</sub> produced in TiO<sub>2</sub> + Pt/TiO<sub>2</sub> mixtures at pH 2 (compare dotted curve to curve 1 in Figure 5). The electron transfer between TiO<sub>2</sub> particles and Pt deposits occurs directly and not through the MV<sup>++</sup> radicals. The formation of larger conglomerates between TiO<sub>2</sub> and Pt/SiO<sub>2</sub> particles cannot be excluded a priori, but probably is of minor importance. Since electron transfer from the TiO<sub>2</sub> particle cannot take place through the silica particle to reach Pt deposits, the mobility of these particles seems to be essential to accomplish successively both electron trapping and water reduction on catalyst surface.

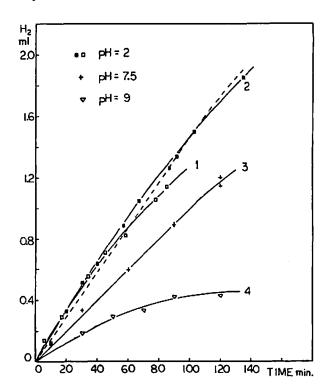


Figure 5. — Dependence of  $H_2$  production with the illumination time for various suspensions containing  $10^{-3}$  M MV<sup>2+</sup> (- - -) or without MV<sup>2+</sup> (---). (1) 0.1 g TiO<sub>2</sub>+0.1 g Pt (0.63 wt. %)/SiO<sub>2</sub>, (2, 3, 4) 0.1 g RuO<sub>2</sub> (0.43 wt. %)/TiO<sub>2</sub>+0.1 g Pt (0.63 wt. %)/SiO<sub>2</sub>.

The presence of small (0.43%) RuO<sub>2</sub> deposits on the surface of TiO<sub>2</sub> particle has improved H<sub>2</sub> production at neutral pH values (see curves 3 and 4 in Figure 5 and compare with respective curves in Figure 4). This result is in agreement with the decrease of the photocurrent and of  $\Delta i/\Delta t$  values by RuO<sub>2</sub> deposits and show that RuO<sub>2</sub> is a good catalyst for H<sub>2</sub> formation.

The formation of  $H_2$  was significantly enhanced when platinum was deposited directly on  $TiO_2$  particles (compare curve 1 with dotted curve in Figure 6). Moreover, when the initial pH was increased from 2 to 10, the amount of  $H_2$  was significantly increased (see Fig. 6). Clearly, photoproduced electrons are trapped more easily by Pt deposits on the  $TiO_2$  surface than by those on separate  $SiO_2$  particles. Even a proton concentration as low as  $10^{-10}$  M was enough to allow efficient  $H_2$  evolution on  $Pt/TiO_2$ , while no  $H_2$  was observed for  $TiO_2 + Pt/SiO_2$  mixtures at pH < 7.

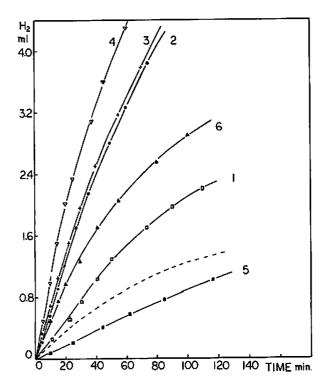


Figure 6. — Comparison between the  $H_2$  evolution versus illumination time for mixed suspensions (---)  $0.1 \,\mathrm{g\,TiO_2} + 0.1 \,\mathrm{Pt}$  (0.63 wt. %)/SiO<sub>2</sub> with those of loaded particles (----)  $0.1 \,\mathrm{g\,Pt}$  (0.63 wt. %)/TiO<sub>2</sub> curves 1. – pH 2; 2. – pH 5.2; 3. – pH 7; 4. – pH 10, or  $0.1 \,\mathrm{g\,Pt}$  (0.63 wt. %)/RuO<sub>2</sub> (0.42 wt. %)/TiO<sub>2</sub>, curves 5. – pH 2; 6. – pH 5.2.

A more efficient hole scavenging action of D-glucose at higher OH<sup>-</sup> concentrations explains the increasing order of curves 1, 2, 3, and 4 in Figure 6. A 0.43 wt. % RuO<sub>2</sub> deposit on TiO<sub>2</sub> particles loaded by 0.63 wt. % Pt significantly decreased the amount of the photoreduced H<sub>2</sub> at pH 3 and pH 5.2 (see curves 5 and 6 in Figure 6). This suggests a decrease of the adsorption of glucose, a decrease in the rate of photooxidation of D-glucose by the photoproduced holes, or blockage of light absorption by the RuO<sub>2</sub> deposits.

#### Conclusions

A combination of both electrochemical and gas chromatography measurements was necessary to elucidate the behavior of illuminated TiO2 particles in aqueous D-glucose suspensions at different pH values. These observations are briefly summarized as follows: (1) The efficiency by which D-glucose reacts with photoproduced holes in illuminated aqueous TiO2 suspensions increases with the OH<sup>-</sup> concentration. (2) H<sup>+</sup> produced during the continuous photooxidation of D-glucose can be removed by using an appropriate catalyst for H<sub>2</sub> production to maintain a constant pH value and thus a high photoactivity. (3) Significant electron transfer between the negatively charged TiO<sub>2</sub> particles after irradiation and platinum deposits on SiO<sub>2</sub> particles occurs, if the proton concentration is sufficiently high to favor the catalytic consumption of these electrons in water reduction. (4) The presence of Pt deposits on the TiO2 surface greatly improves their electron trapping action and promotes H2 production at alkaline pH values, where the hole scavenging action of D-glucose is favored.

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